

Dynamics of spin and orbital phase transitions in YVO_3

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YVO_3 exhibits a well separated sequence of orbital and spin order transitions at 200 K and 116 K, followed by a combined spin-orbital reorientation at 77 K. It is shown that the spin order can be destroyed by a sufficiently strong optical pulse within less than 4 ps. In contrast, the orbital reordering transition from C -type to G -type orbital order is slower than 100 ps and goes via an intermediate nonthermal phase. We propose that the dynamics of phase transitions is subjected to symmetry relations between the associated phases.

Dynamics of phase transitions is an important and rapidly growing area of modern science. The interest in this topic is not only limited to condensed matter community, but also touches other areas of science ranging from geology [1] to modeling of traffic dynamics [2]. At the same time, the exponential growth of publications in this area is also driven by applications in optical switching [3] and phase-change data storage [4] where throughput is ultimately limited by the phase-change rate. It has been demonstrated that some optically induced structural [5, 6, 7, 8], charge [9, 10], orbital [11], and spin order phase transitions [12, 13, 14] may occur on pico- and sub-picosecond time scales, much faster than phonon-phonon or even electron-phonon equilibration times. Up to now research on the dynamics of so-called nonthermal phase transitions has mainly been focused on single phase changes. This paper address the question on how and which phase transitions can occur in materials that allow several phase changes.

An excellent material to pursue this goal is the perovskite YVO_3 , which shows a sequence of orbital and spin transitions as a function of temperature. At room temperature this crystal is paramagnetic and has an orthorhombic $Pbnm$ structure. At $T_{OO} = 200$ K, the material undergoes a second order transition into an orbitally ordered phase, in which the d_{xz}/d_{yz} orbital occupation alternates in all three crystallographic directions (G -type ordering) [15, 16]. This transition is accompanied by a symmetry lowering into a $P2_1/b11$ monoclinic form [17] with a continuous expansion along the b axis and a contraction along the a and c axes [18]. Below another second order transition at $T_N = 116$ K the spins form an antiferromagnetic arrangement in the ab plane with a ferromagnetic arrangement along the c axis (C -type ordering). Finally, at $T_{CG} = 77$ K, YVO_3 undergoes a first-order phase transition, changing the spin ordering from C - to G -type with a simultaneous change in the orbital ordering from G - to C -type. This phase transition is accompanied by an abrupt magnetization reversal along the a axis [15, 19] and, quite unusually, increases the symmetry [20] of the lattice back to the orthorhombic $Pbnm$ form [16, 17, 21, 22, 23]. All three phase transitions manifest themselves as pronounced changes in the optical

absorption in three spectral bands associated with $d-d$ transitions and located at 1.8 eV, 2.4 eV, and 3.3 eV [17]. This allows for tracing the dynamics of the phase transitions by monitoring the optical reflectivity [17]. Recently, optically induced nonthermal melting of the orbital ordering was reported in LaVO_3 [11]. This material has a phase diagram similar to YVO_3 . An important difference is that T_{CG} and T_{OO} in LaVO_3 are so close to each other that the different phases are not distinguishable in optically induced experiments. This Letter reports a study of optically induced phase transitions of the orbital and spin order in YVO_3 . In particular, it is shown that optically induced spin melting and orbital reordering occur on different time scales, which is ascribed to a difference in symmetry changes during the phase transitions.

Time resolved two color pump-probe experiments have been performed on bc -oriented polished platelets of an YVO_3 single crystal placed in a helium-flow cryostat. The details of the sample growth can be found in Ref. [17]. The optical pump and probe pulses were derived from an amplified Ti-sapphire laser with a repetition rate of 1 kHz, in a combination with an optical parametric amplifier. In order to ensure quasi-homogeneous excitation of the sample, the pump wavelength was set to 800 nm (1.55 eV), which is slightly below the band gap of YVO_3 . For probing, a wavelength of 630 nm (1.97 eV) was chosen, since at this wavelength the reflectivity is sensitive to all the phase transitions.

Figure 1 displays some typical time traces of the transient reflectivity for different excitation power densities at $T = 25$ K, i.e. in the C -type orbitally ordered phase. All traces show an abrupt change just after arrival of the pump pulse followed by a kinetics with pronounced temporal oscillations in the transient reflectivity with a period of about 19 ps [24]. These oscillations are the result of the interference of the probe light reflected from the sample surface and from the acoustic strain wave formed by an optically induced stress [25]. This acoustic wave propagates in a direction perpendicular to the surface with the velocity $s = \lambda_{\text{probe}}/2n\tau_{os}$, with n the refractive index of YVO_3 , λ_{probe} the wavelength of the probe light, and τ_{os} the oscillation frequency in the reflectivity. Using our experimental data $\tau_{os} = 19$ ps (Fig. 1) and

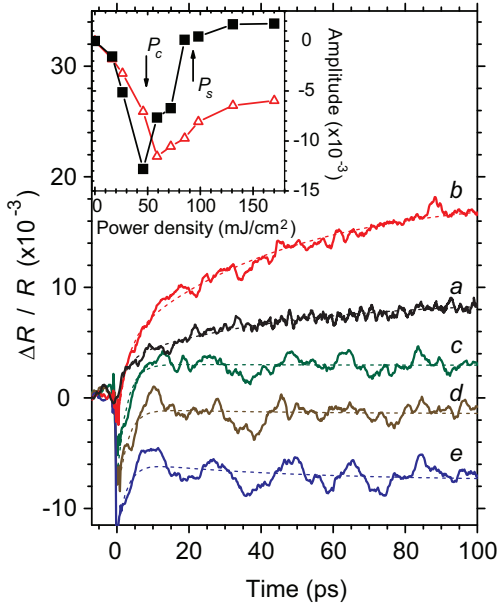


FIG. 1: (Color online). Dynamics of the transient reflectivity of YVO₃ following optical excitation with a power density of (a) 25 mJ/cm², (b) 45 mJ/cm², (c) 85 mJ/cm², (d) 100 mJ/cm², and (e) 170 mJ/cm². Solid lines show the experimental data measured at 25 K, dotted lines are a fit of a double exponential function to the experimental data. The inset shows the amplitude of the fast (\triangle) and slow (\blacksquare) decay components of the transient reflectivity extracted from the fits as a function of the excitation power density.

knowing [17] $n = 2.3$ at $\lambda_{\text{probe}} = 630$ nm we are able to estimate $s = 7.2 \pm 0.5$ km/s, which is close to the longitudinal sound velocity measured in another vanadate perovskite [26]. Further investigation of the acoustical properties of the YVO₃ are outside the scope of the present research and, hereafter, our discussion will be focused on the non-oscillation part of the transient reflectivity dynamics, which can be quite faithfully fitted with a double-exponential decay function with $\tau_1 = 2.7 \pm 1$ ps and $\tau_2 = 45 \pm 10$ ps for fast and slow decay terms, respectively.

For weak optical excitation [Fig. 1, curves a and b] the slow decay dominates the transient reflectivity dynamics, at late times the transient reflectivity is positive and rises with increasing the excitation power density. However, when the excitation power density, P , overcomes a critical power density, P_c , the slow decay component suddenly disappears [Fig. 1 curves c-e]. Moreover, the saturation level for the transient reflectivity now becomes more and more negative for stronger excitation. We found that P_c is virtually independent of the initial lattice temperature, as long as $T < T_N$, but depends strongly on the excitation wavelength and varies from $P_c = 55$ mJ/cm² to $P_c = 3$ mJ/cm² for the pump wavelength set to 800 nm and 400 nm, respectively. This is most probably due to a substantial change in the ab-

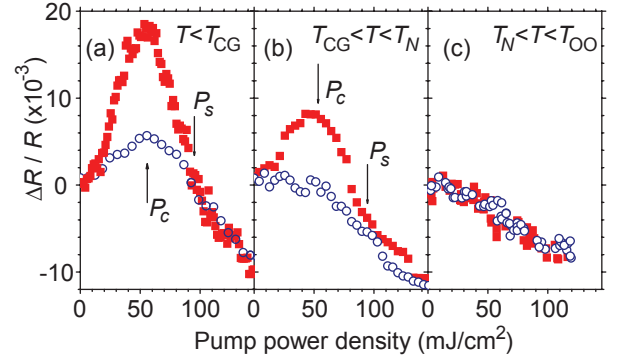


FIG. 2: (Color online). Dependence of the transient reflectivity on the pump power density probed at 4 ps (\circ) and at 100 ps (\blacksquare) after the optical excitation at (a) $T = 50$ K, (b) $T = 100$ K, and (c) $T = 140$ K.

sorption varying by about an order of magnitude in this spectral range [17]. The drastic change in the transient reflectivity dynamics at $P = P_c$ is vivid in the inset to Fig. 1, which plots the amplitudes of transient reflectivity decay components as a function of the pump power density. Upon increasing the excitation power density the amplitude of the slow decay (solid squares) grows linearly up to $P = P_c$, after which it rapidly decreases until it vanishes at $P_s = 1.7P_c$. In contrast, the amplitude of the fast decay (open triangles) remains quite sizeable even for $P > P_s$.

The observed threshold behavior provides direct evidence for a *photoinduced phase transition*. In order to assign this transition to a specific phase change the power dependence of the transient reflectivity has been measured starting out from the three different phases of YVO₃: the *C*-type orbital ordered phase at $T = 50$ K [Fig. 2(a)], the *G*-type orbital ordered phase with *C*-type spin order at $T = 100$ K [Fig. 2(b)], and the *G*-type orbital ordered phase with disordered spins at $T = 140$ K [Fig. 2(c)]. The data are presented for two important delays: at 4-ps delay, just after the fast τ_1 -dynamics ends (open circles), and at 100-ps delay, when the transient dynamics is over and the reflectivity has reached a plateau (solid squares). The photoinduced phase transition manifests itself as a kink at $P = P_c$ [Fig. 2(a,b)], which appears below T_N only. Quite importantly, the shape and the threshold in the power dependence does not change when the sample temperature crosses T_{CG} . However, when the temperature approaches T_N from below, the kink in the power dependence diminishes [Fig. 2(b)] and finally disappears at $T = T_N$. For $T > T_N$ the transient reflectivity has a monotonic linear dependence on the excitation power density [Fig. 2(c)]. The temperature dependence of the transient reflectivity is plotted in Fig. 3 for two important excitation regimes: (a) $P < P_s$, and (b) $P > P_s$. In the high excitation regime these dependencies show a kink at $T = T_N$ both for 4 ps and for

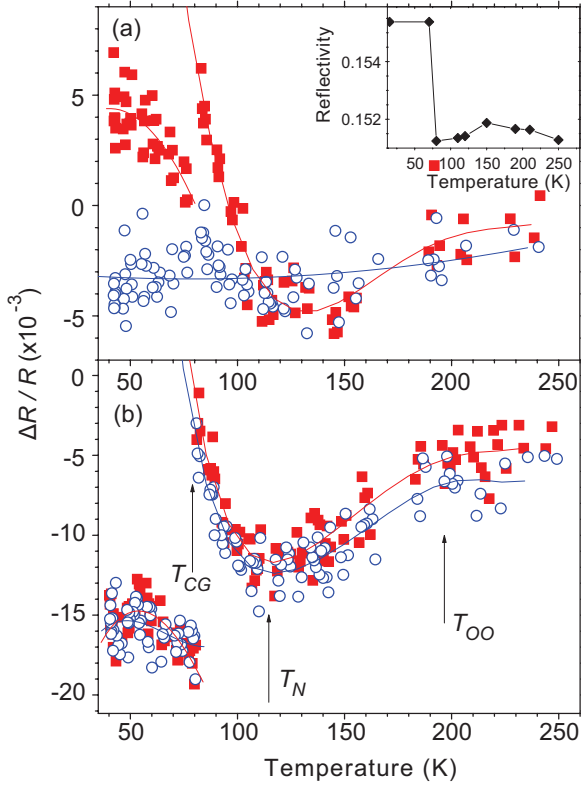


FIG. 3: (Color online). Temperature dependence of the transient reflectivity probed at 4 ps (\circ) and 100 ps (\blacksquare) for (a) 85 mJ/cm² and (b) 190 mJ/cm² excitation power density. Lines are guided for eye. Inset shows the stationary reflectance calculated using the optical constants taken from Ref. [17].

100 ps delays. In the weak excitation regime the kink in the temperature dependence is notticable only in the 100-ps trace, but at the same temperature as in the strong excitation regime confirming that the background sample temperature is not affected by the optical excitation.

The disappearance of the threshold power behavior above $T = T_N$ indicates that the observed photoinduced phase transition is related to the *melting of the spin order*. This conclusion rises an interesting question on whether the optically induced phase is thermodynamically favorable (thermal) or not. The answer to this question may be deduced from a comparison of the optically induced changes in the reflectivity and the variation of the reflectivity observed at different thermal phases. The stationary reflectivity of YVO₃ is plotted in the inset to Fig. 3(a). First, we compare the reflectivity changes for $T > T_{CG}$. Here, the stationary reflectivity increases in the spin ordered and decreases in the spin disordered states with elevated temperature. Hence, the thermally induced change in the reflectivity is positive in the spin ordered ($T_{CG} < T < T_N$) and negative in the spin disordered states ($T_N < T < T_{OO}$). In turn, for $P < P_c$, the optical excitation of the spin ordered state induces a pos-

itive change in the reflectivity at 100 ps delay [Fig. 2(b), solid squares]. However, for $P > P_s$, at which the optical excitation destroys the spin order, the transient reflectivity becomes negative. Further, the transient reflectivity of the spin disordered state is negative for any excitation power densities [Fig. 2(c)]. The thermally-driven changes in the reflectivity thus coincide with the optically induced changes measured at 100 ps delay [Fig. 2(b) and (c), solid squares] signifying that at 100 ps after the optical excitation the spins and electronic subsystems has reached the thermodynamic equilibrium.

We now turn to the discussion over the transient reflectivity below the spin-orbital reorientation transition. This transition manifests itself by a substantial decrease in reflectivity [inset to Fig. 3(a)]. However, the optically induced changes in reflectivity are positive up to the spin melting threshold [Fig. 2(a), $P < P_c$]. This indicates that at $T < T_{CG}$ the arrangement of spins and orbitals are far from thermal equilibrium even 100 ps after the optical excitation.

The reported experimental data suggest the following model. In our experiment the pump pulse excites the electronic transition from the oxygen 2p band to the empty states in the vanadium 3d band. Subsequently, these electrons relax to lower energy states and their excess energy excites the spin and orbital degrees of freedom. For $T > T_N$ the change in the reflectivity of YVO₃ is governed by an arrangement of the orbital occupation, which thermalizes within a time τ_1 . In addition, at $T < T_N$, the photoexcited hot electrons may also transfer their energy to the ordered spin network. At $P < P_c$, the subsequent thermalization of the spins manifests itself as the slow (τ_2) component in the transient reflectivity traces. The increased spin temperature and excited orbitals influence reflectivity in opposite directions that leads to a kink at $T = T_N$ in the temperature (Fig. 3) and power dependencies [Fig. 2(a) and (b)] of the transient reflectivity. Another consequence of the rapid disordering of the spin network is disappearance of the slow decay component in the reflectivity kinetics for $P > P_s$, suggesting that the optically induced melting of the spin order is nonthermal. The dynamics of the spin-orbital reordering transition is radically different. As it has been mentioned, below the first order phase transition the arrangement of the orbitals remains to be far from the equilibrium even 100 ps after the optical excitation. However, even in this initial phase a strong optical excitation may still promote a melting of the spin order in less than 4 ps. Indeed, for $P > P_s$ the transient reflectivity measured at 4 ps and 100 ps delays coincide with each other [Fig. 3(b)]. This leads to a conclusion that the $C \rightarrow G$ orbital transition does not occur on a picosecond time scale and YVO₃ undergoes to a metastable phase with disordered spins but C -ordered orbitals.

We suggest that the striking difference in the transition dynamics of the spin and orbital reordering and the

spin disordering transitions is related to their symmetry change. The rapid spin melting leads to an increase in the spin network symmetry. Oppositely, the spin and orbital reordering is accompanied by a lowering of the lattice symmetry, which requires a considerable time to synchronize the new ordering across the excited volume. More generally, a symmetry rule that restricts the speed of phase transition kinetics can be formulated as follow: *The transition rate from a phase with symmetry group α to a phase with symmetry group β is limited if α is not a subgroup of β ($\alpha \not\subseteq \beta$)* and the limiting factor for breaking a symmetry is the time required to pass the information about the new arrangements over the excited volume, e.g. it is limited by the propagation velocity of phonons for a structural change. We suggest that the proposed symmetry rule may be valid for any kind of phase transition unless the excitation creates a coherent wave that breaks the symmetry itself. To the best of our knowledge, all reported experimental observations thus far are in agreement with this rule. Indeed, up-to-date reported ultrafast solid-to-liquid [5, 6, 7], solid-to-solid [3, 8, 9], charge [10], orbital [11], and spin transitions [12, 13] are accompanied by $\alpha \subseteq \beta$ symmetry changes. Oppositely, the phase transitions that obey $\alpha \not\subseteq \beta$ symmetry changes, e.g. amorphous-to-crystalline transition in GeSb films [27], paraelectric-to-ferroelectric transition in tetrathiafulvalene-*p*-chloranil [28], and the spin transition in an organometal spin-crossover material [29] were reported to be slow.

In conclusions, we demonstrated that the dynamics of the photoinduced spin disordering transition in YVO_3 has a power threshold and occurs on a time scale faster than 4 ps. In contrast, the orbital reordering transition from *C*-type to *G*-type orbital order was not observed on the picosecond time scale suggesting that it is slower than 100 ps. We suggest that the difference in the dynamics of these phase transitions may be explained by their symmetry change and proposed a ‘symmetry’ rule, which put a general restriction on phase transition dynamics. This rule may prove to have some useful implication, i.e. it limits rates of certain bidirectional phase switching, which is important to consider in designing ultrafast phase change devices.

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